ANL/ES-115, Vol. 2

Wastewater and Sludge Control-Technology Options for Synfuels Industries

Volume 2: Tar-Sand-Combustion Process Water—Removal of Organic Constituents by Activated-Sludge Treatment

M. F. Torpy, L. A. Raphaelian, and R. G. Luthy

ARGONNE NATIONAL LABORATORY
Energy and Environmental Systems Division

prepared for
U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A04
Microfiche copy: A01

Distribution Category:
Oil Shales and
Tar Sands (UC-91)

ANL/ES-115, Vol. 2

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Argonne, Illinois 60439

WASTEWATER AND SLUDGE CONTROL-TECHNOLOGY OPTIONS FOR SYNFUELS INDUSTRIES

VOL. 2: TAR-SAND-COMBUSTION PROCESS WATER -- REMOVAL OF ORGANIC CONSTITUENTS BY ACTIVATED-SLUDGE TREATMENT

by

M. F. Torpy, L. A. Raphaelian, and R. G. Luthy*

Energy and Environmental Systems Division
Applied Geoscience and Engineering Group

November 1981

work sponsored by

U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Environmental Protection, Safety,
and Emergency Preparedness
Office of Environmental Compliance and Overview

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PREFACE

This report is part of a series of studies of wastewater and sludge control-technology options for synfuels industries. Presented here is an analysis of control-technology options for process waters associated with the recovery of tar sand oil products resulting from a reverse-forward combustion experiment. Other reports in the series deal with wastewaters from lignite gasification and from in-situ production of oil from oil-shale kerogen.

The Argonne National Laboratory synfuels wastewater environmental control-technology program is a coordinated effort among Argonne, industrial, academic, and consulting-firm specialists in such technology. All work is supported by the Environmental Control Technology Branch, Environmental and Safety Engineering Division, Office of Environmental Compliance and Overview, under the Department of Energy's Assistant Secretary for Environmental Protection, Safety, and Emergency Preparedness. The DOE project officer for this report is Henry Walter.

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ACKNOWLEDGMENTS

Our gratitude is extended to Drs. Basil Mercer and Anthony D. Toste, Battelle Pacific Northwest Laboratory, for their critical review of, and much-appreciated comments on, the manuscript. Dr. Sydney Bourne of the Argonne Analytical Chemistry Laboratory directed the task of extracting and preparing the samples for analysis; Dr. Meyrick J. Peak, Biological and Medical Research Division, Argonne, directed the analysis of the sample for mutagenicity; Mr. Dan Jenkins, of the Department of Civil Engineering at Carnegie-Mellon University (C-MU), operated the activated sludge unit; Ms. Helen Cordy, C-MU, provided the scheduled analysis of the wastewater treatment parameters; and Tom Spedding and Carl Roosmagi, both of the Division of Environmental Sciences, Laramie Energy Technology Center, provided the composite sample and the analytical data on the sample.

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ABSTRACT

Gas-chromatography/mass-spectrometry analysis of raw process water from reverse-forward combustion in a tar sand extraction experiment indicated that identifiable compounds were distributed in about equal portions among acid, base, and neutral fractions. The compounds in the neutral fraction were unsaturated, oxygenated methyl cyclohexenyl ketones, methyl-methylcyclohexenyl ketones, acetophenones including methyl-tolyl ketones, lactones, and indanones. Neutral fraction constituents were reduced by about 99% during activated-sludge treatment. The base fraction consisted of pyridines, quinolines and their alkane substitutes, and acridines. These compounds were reduced by about 76% during treatment. The acid fraction consisted of carboxylic acids ranging in molecular weight from C_1 to C_{11}, phenols and cresols, and benzoic and toluic acids. These materials were reduced by about 95% through activated-sludge treatment. It was concluded that (1) activated-sludge treatment can reduce soluble organic carbon and chemical oxygen demand by about 90% in the process water and (2) the water is nonmutagenic as defined by the standard Salmonella/Ames test.

EXECUTIVE SUMMARY

This study of organic characterization and water treatment was designed to investigate the treatment and organic-constituent reduction of materials in process water generated from an in-situ experiment using reverse-forward combustion of tar sand. The water treatment consisted of biological oxidation with activated sludge, and the organic-constituent analysis included concentrating and separating the organic material into fractions and analyzing them by gas chromatography/mass spectrometry. The raw influent sample was also screened for mutagenicity by the Salmonella/Ames test.

The activated-sludge reactor was operated as a continuous-mixed, stirred reactor with a hydraulic detention time of 6 days and a mean cell-residence time of 40 days. The pH of the process water was adjusted to about 3.9-4.5 in order to maintain a reactor liquor pH of 7, and phosphorus was added to insure an adequate nutrient level in the liquor.

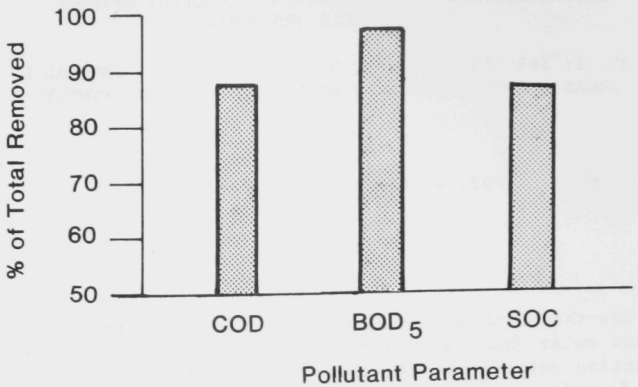


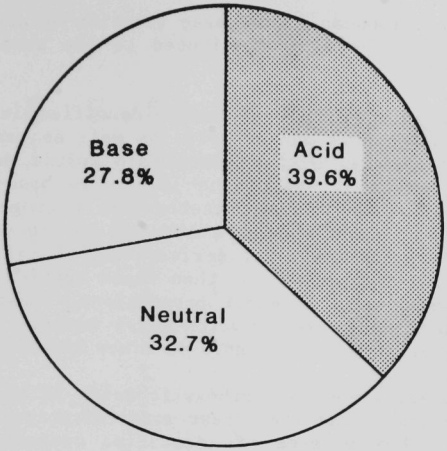
Fig. 1 Effect of Activated-Sludge Treatment in Reducing Chemical Oxygen Demand, Biological Oxygen Demand, and Soluble Organic Carbon in Process Water

Activated-sludge treatment reduced the process water's chemical oxygen demand (COD) by 88%, biological oxygen demand (BOD_5) by 97%, and soluble organic carbon (SOC) by 88% (see Figure 1). In addition, the treatment achieved reductions in color of 91% and reductions in ammonia concentration of 90% (as nitrogen), with a concomitant increase in nitrates. In general, activated sludge was found to be an effective method for reducing the organic content of process water from tar sand combustion, and good solids-settling characteristics also result from this treatment.

Raising the pH of the water was found to cause the slow formation of a poor-settling "wispy" coagulated material that contributed 57% of the total organic carbon of the untreated water. It was determined from settling tests that simple settling methods would be impractical as pretreatment alternatives to removal of this material. Although the coagulated material was not removed before the activated-sludge treatment was begun, it did not appear to impair biological oxidation. Limited testing with various solvents possessing properties that ranged from nonpolar to polar showed that solvent-extraction pretreatment was impractical for efficiently reducing the concentration of the chemical oxygen demand in the process water.

The organic constituents were separated into acid, base, and neutral extract fractions. These extracts contained approximately equal total mass concentrations (Figure 2) when analyzed as extractable/chromatographable compounds. The principal organic constituents were determined to be unsaturated nitrogenous and oxygenated heterocyclics and carboxylic acid compounds, most of which were probably formed during tar sand combustion.

Of the three fractions, the neutral fraction appears to be especially receptive to biological oxidation (99% reduction); material in the acid fraction was also reduced effectively (95%). Activated sludge reduced the con-



Total: 44.2 mg/L

Fig. 2 Extractable/Chromatographable Organic Fractions in Process Water

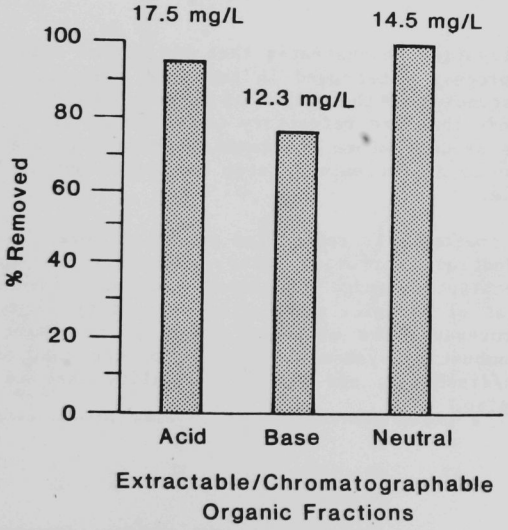


Fig. 3 Reduction of Extractable/Chromatographable Organic Fractions in Process Water by Treatment with Activated Sludge

centration of organic compounds in the base fraction by about 76% (see Figure 3); the lower efficiency here is attributed to the presence of refractory nitrogenous heterocyclics.

As shown in Figure 4, the compounds identified in the acid fraction consisted primarily of phenols and cresols, as well as carboxylic acids with molecular weights as high as C_{11}. Benzoic and toluic acids were found in minor proportions. More than 99% of the identified base-fraction constituents were identified as single-ring heterocyclic nitrogen compounds, e.g., pyridine and its alkyl substitutes; and fused heterocyclic nitrogen compounds, e.g., quinoline and its alkyl derivatives. Single-ring heterocyclic compounds were somewhat more prevalent than fused heterocyclic nitrogen compounds. Acridines were found in minor proportions. Most of the identified neutral-fraction constituents were cyclohexenyl ketones. Lactones, acetophenones, and indanones were constituents of minor concentration.

The higher-molecular-weight carboxylic acids in the acid fraction and the quinolines in the base fraction appear more refractory to biological oxidation than do the other classes of identified compounds (see Figure 5). Acridines in the base fraction may also tend to be refractory, but their estimated low concentrations makes difficult an accurate description of their removal efficiency. All compounds in the neutral fraction of the effluent were present in very low concentrations, and a close correlation of the resulting constituents with those of the influent could not be demonstrated.

The process water influent was tested at two different doses with two strains of bacteria in the standard Salmonella/Ames test and was found to be nonmutagenic.

This investigation demonstrates that biological oxidation is a treatment option for process water used in tar sand combustion; the study also provides an understanding of the nature of organic materials in the water and of organic compounds that are refractory to activated-sludge treatment. Adjustment of pH is needed before treatment with activated sludge can begin. Solvent extraction as a pretreatment step is judged not to be warranted nor especially feasible.

Biological treatment is recognized as one of several options available for residuals reduction in process water. The kinetics and optimal design parameters for activated-sludge treatment were not investigated. Other methods for removal of organics may include a variety of physical and chemical treatment processes. The ultimate choice of treatment for a tar sand reverse-forward combustion system will depend on the cost of treatment, options for recycle/discharge, and the water quality that is required in the water management plan.

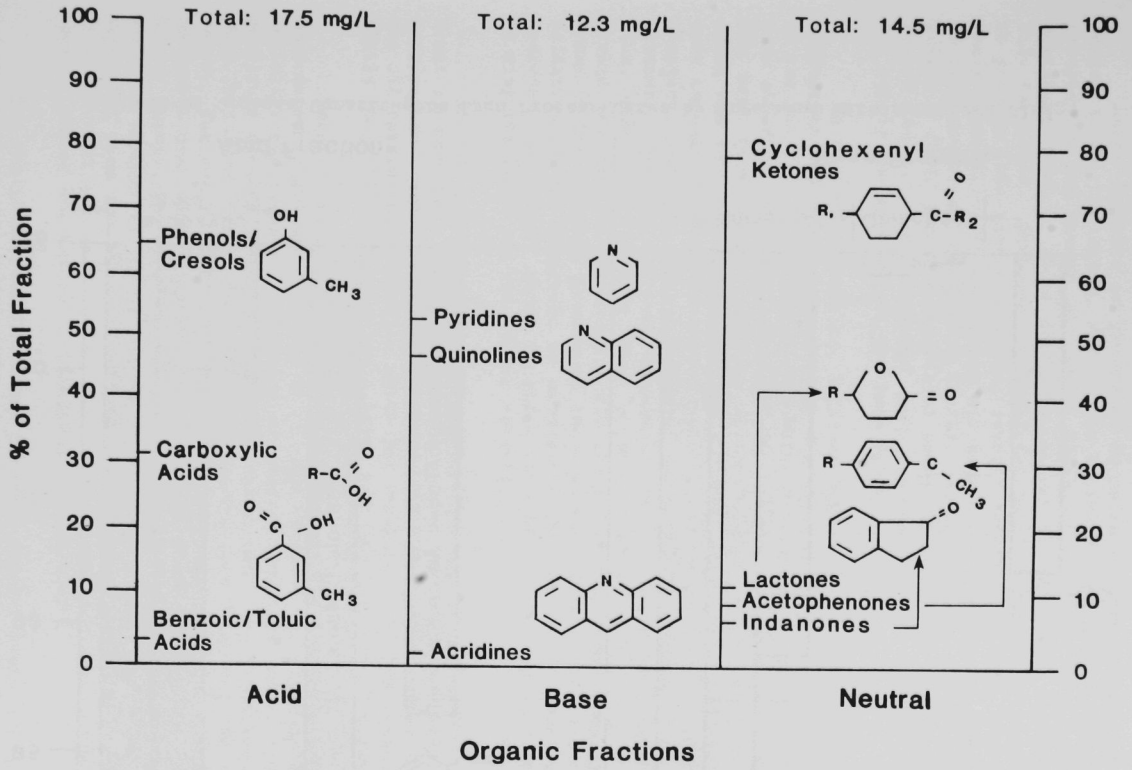


Fig. 4 Organic Constituents Identified in Each Fraction of Process Water

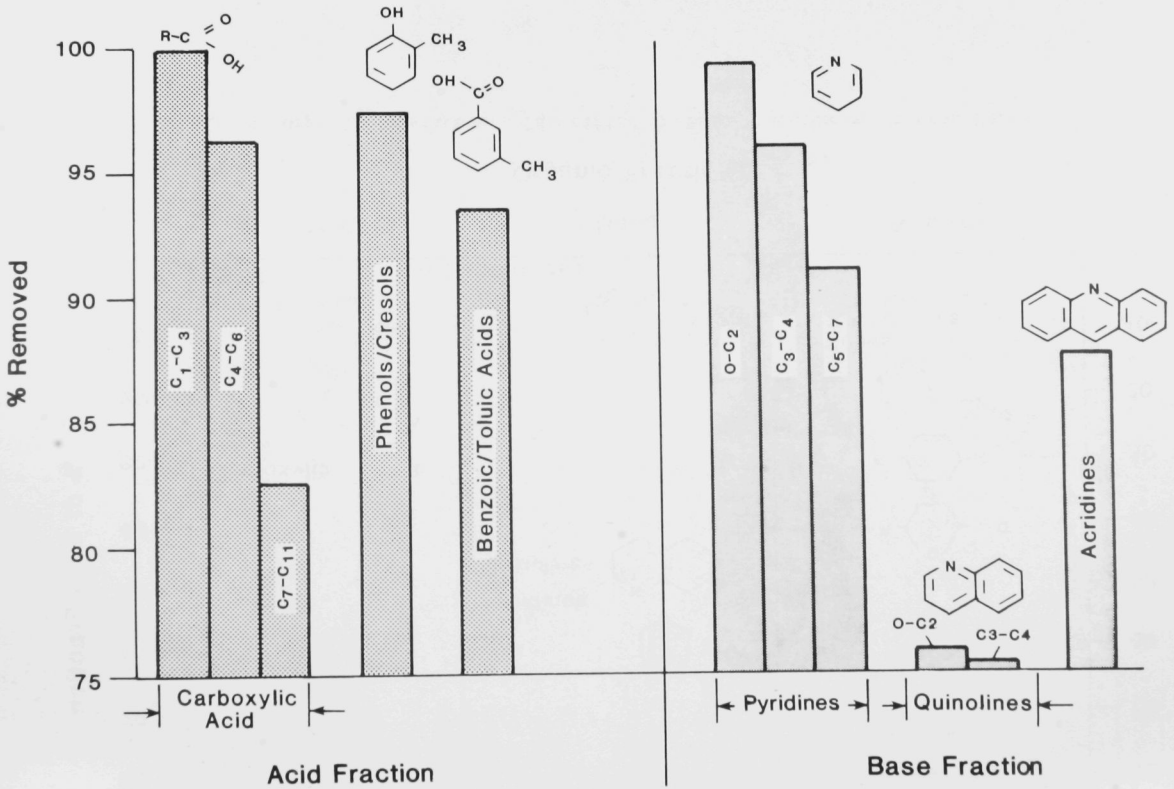


Fig. 5 Removal of Organic Constituents from Process Water by Treatment with Activated Sludge

1 INTRODUCTION

Large deposits or groups of deposits of oil-impregnated rock are referred to as tar sands, and in the United States these deposits are mainly grouped in and around the Uinta Basin of northeast Utah and in central-southeast Utah.[1] These deposits consist of 90 to 95% of the total mapped U.S. tar sands. Although no commercial facility presently exists in the U.S. to process this energy resource, several technologies have been evaluated for their feasibility in extracting oil from tar sands. Among these technologies is reverse-forward combustion (R-FC). An in-situ extraction method, R-FC requires a field pattern of drilled holes to supply air for combustion and to remove the oil. A successful R-FC process requires careful control of the air supply and movement of the burn front.

In reverse combustion, ignition begins at the production well and the combustion front moves toward the air injection well in a direction counter to the air flow. Movement of the burning front is a function of heat conduction ahead of the front. Some of the bitumen is burned, and coke is left in the sand from thermal cracking of the bitumen. Reverse combustion in tar sands has two main advantages over forward combustion: (1) vaporized fluids move through the hot, burned-out part of the reservoir with no possibility of plugging, and (2) the oil produced is of higher quality than the original bitumen. However, reverse combustion is relatively more sensitive to air flux, which must be kept above a defined minimum or the process may turn around and burn in the forward direction. Also, spontaneous ignition might occur in the unburned portion of the reservoir as a result of low-temperature oxidation if air injection is maintained for too long.[2] Reverse combustion precedes the forward phase in order to minimize the tendency of the bitumen to plug the pores and retard oil recovery.

In the subsequent forward-combustion step, the direction of the burn front is reversed, moving toward the production wells and away from the air supply. Hot combustion gases heat the oil ahead of the flame front and push the oil toward the production wells for recovery. Forward combustion is more easily controlled and requires a lower air flux than does the reverse process.

Water is considered a scarce resource in the region where the U.S. tar sand deposits are located, and it is thus necessary to understand the characteristics and treatment potential of process water in order to recognize the available options for water discharge and reuse. For these reasons, studies were initiated to characterize and to evaluate treatment of R-FC process water. The water studied in this project was collected from R-FC experiment conducted near Vernal, Utah, in late 1977 through early 1978 by the Laramie Energy Technology Center (LETC).[3] Steam was injected into the production wells to assist in recovering the viscous products. The water sample was separated from the oil product and stored as an unfiltered sample at LETC, from where it was distributed for analysis and treatment. The LETC sample control number was marked 77-(TARSANDS-2C)-OOW-OO-U.

The analytical and treatment research project described in this report was designed to characterize the organic constituents of the tar-sand-combustion process water, and to determine the feasibility of using conventional physical-chemical and biological treatment methods for reducing the organic

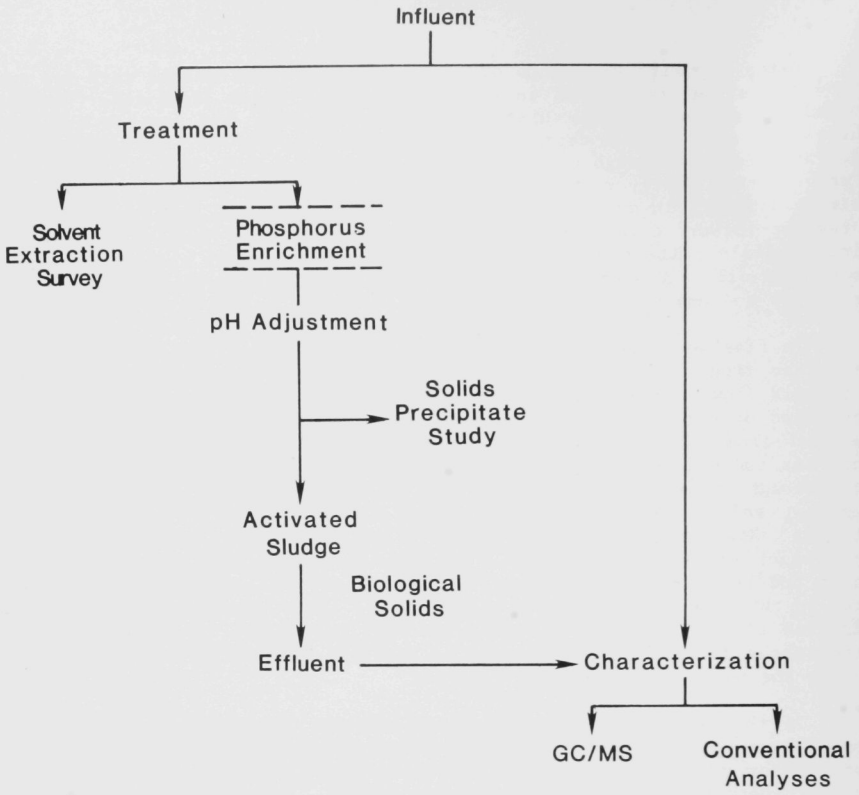


Fig. 6 Flow Diagram Showing the Analytical and Treatment Study of Process Water from Tar Sand Combustion

concentration of the water. A flow diagram describing the research project is provided in Figure 6. The treatment work was complemented by conventional wet chemical analyses, detailed gas chromatography/mass spectrometry (GC/MS) analyses, and mutagenicity testing. The focus of the study was on the use of activated sludge for removing organic material from the tar-sand-combustion process water. Solvent extraction, pH adjustment and precipitation, and polymer coagulation were also evaluated for their potential in removing organic material during pretreatment.

2 ANALYTICAL PROCEDURES

2.1 ORGANIC CONSTITUENTS

The influent to the activated sludge treatment and the effluent from the treatment were prepared for GC/MS analysis by separating and concentrating the organic content into acid, base, and neutral fractions. The preparation procedure was by solvent extraction with methylene chloride. The solvent extraction methodology is described in Appendix A. The GC/MS analysis was performed on aqueous-phase samples that had been filtered through "Mead Flo" glass-fiber filters.

2.1.1 Equipment and Operating Conditions

In order to study the organic constituents extracted from the aqueous phase of the process water samples, capillary-column GC/MS was used to identify the organic constituents, and capillary-column GC was used to quantify the major components. Quantification was based on a set of standard compounds that were representative of those found in the sample extracts.[4]

The gas chromatograph used in this study was a Hewlett-Packard (HP) 5840 fitted with cryogenic cooling with liquid carbon dioxide, extra peak storage for integrated areas of up to 500 peaks, and a second-generation HP capillary-column injection port (18835B), which is a modification of the Grob-type splitless injection system. An automatic sampler (HP 7661) was used, and the injection amount was set at either 1 or 3 L. The capillary column was an HP 50-m fused silica Carbowax 20M with a quoted maximum operating temperature of 220°C. The oven temperature was programmed to increase at 2°C/min from 20 to 220°C with a 2-min hold at 20°C and an 18-min hold at 220°C. The injection port temperature was 225°C and the flame ionization detector temperature was 250°C. Operating conditions for the GC portion of the GC/MS were the same as those used in the GC-only runs; the injection port temperature was 225°C and the column was an HP 50-m fused silica Carbowax 20M.

The data system used in this study was an HP 5930 equipped with an HP 5933A computer with a 16K, 16-bitword core memory, a 7900A dual disc drive with two 2.5M-byte discs (one fixed and one removable), and a Tektronix 4012 graphic display terminal. Peripheral equipment included a Tektronix 4631 hard-copy unit. Data collection was done with a standard software package provided by Hewlett Packard and known as the AQUIRE program; analysis was done with Hewlett Packard's SPEED program. The mass range scanned was 35-350 AMU, and two analog-to-digital (A/D) measurements were made for each datum point (each 0.1 AMU); cycle time was approximately 2 sec.

Standards used in determining response factors and reproducibility of the HP 5840 GC were obtained from Aldrich Chemical Company (Milwaukee, Wis.), Eastman Kodak Company (Rochester, N.Y.), and Fischer Scientific Company (Fair Lawn, N.J.).[5]

2.1.2 Methods Used for Identification and Quantification

Each of the fractions was analyzed on the GC using a split ratio of approximately 20 and an injection volume of 1 μL. Each GC chromatogram was then studied in order to guide the subsequent analysis. When the chromatogram:

1. Was satisfactory, the fraction was used without dilution or concentration for quantification of peaks.
2. Showed overload, the fraction required dilution. An estimate of the dilution required was made and the fraction was rerun at that dilution.
3. Was slightly weak, indicating that an additional small amount of the fraction was required to produce a satisfactory chromatogram, the fraction was then rerun with 3-μL injection and a split ratio of approximately 20.
4. Was very weak, indicating that considerably more of the fraction would be required to produce an acceptable run, the GC injector was changed to a Grob-type splitless injector and a 1-μL sample was injected.
5. Showed the 1-μL splitless injection to be slightly weak; the fraction was run at 3-μL splitless; if found to be very weak, the fraction was concentrated and run at 3-μL splitless.

The GC was used for quantification of the identified peaks and for establishing the quantity, dilution, or concentration of samples. The GC was also used for selecting the injection method required for both quantification of peaks by GC and identification of peaks by GC/MS.

Organic compounds were identified by studying the fragmentation patterns of the mass spectra and the associated retention time and/or by studying the spectra or data in the ASTM Index of Mass Spectral Data,[6] Stenhagen, Abrahamson, and McLaffety's Registry of Mass Spectral Data,[7] and Heller and Milne's EPA/NIH Mass Spectral Data Base.[8] The identified organic compounds were quantified using the integrated areas (area counts) of the HP 5840 GC and the response factors of representative compounds developed in standard runs with split and splitless injection and with 1- and 3-μL injection.[5]

2.1.3 Sources of Error in the Analysis

As in any GC/MS or GC-only analysis of complex mixtures, there are numerous sources of error. First, there is the problem of discrimination in the extraction process or in the recovery step. Liquid-liquid extractions into acid, base, and neutral fractions are inefficient at best. Of greater consequence is the fact that the efficiency varies for different compounds; thus, a single value cannot be factored to correct extraction efficiency for all compounds. In a liquid-liquid extraction where water is one of the components, typically the nonpolar compounds are extracted whereas strongly polar compounds remain in the aqueous phase along with such relatively nonpolar compounds as alcohols, ketones, and mercaptans, which are only partly extracted.

A second source of error in the analysis involves the estimation of response factors for the compounds found in these mixtures. A previous report[4] describes a study done on several compounds in order to establish response factors and reproducibility from run to run. From these results, it can be seen that reproducibility is excellent and is probably within ±10%. However, the response factors vary considerably with the specific compound. The area counts per nanogram for a 1-μL injection, splitless, vary from 452 for pyridine to 1190 for dicyclohexyl. For groups of compounds, the range of area counts per nanogram is more narrow: 452 to 526 for four pyridines, 616-812 for four anilines, 664 for quinoline and 495 for benzylamine. For hydrocarbons, the range is 772 to 984. Thus, the range is not as wide for specific types of compounds and, with the appropriate response factors, errors for individual compounds might be expected to be in the ±20% area.

With splitless injection, approximately 98 ± 2% of the sample injected goes into the column if the injection port is leak-free. With split injection, the split ratio can vary from compound to compound. This variance can be determined by dividing the average count per nanogram for splitless injection by that for split injection. This type of test has shown that the split ratio varies from 19.1 to 24.4 for a series of 14 neutral compounds, and, with the exception of two compounds having split ratios of 14.3 and 12.9, from 17.7 to 19.6 for 11 basic compounds. The amount injected, 1-μL, appeared to have no discernible effect on the split ratio or on the area counts per nanogram.

Thus it appears that although there are variations in the response factors for compounds and in the split ratios, the variations within a group are relatively small. The response factors used in this study are shown in Table 1.

Table 1 Response Factors Used in Calculating Mixture Concentration

Type of Compound	Area Counts per Nanogram	Type of Compound	Area Counts per Nanogram
Neutral		Acid	
Alkanes	830	C_3	16.7
Cyclohexanes	880	C_4	24.8
Cyclic compounds	1040	C_5	35.0
Polar compounds	720	C_6	47.0
		C_7	51.4
Basic		C_8	55.0
Pyridines	480	C_9	52.6
Anilines	690	C_{10}	52.6
Miscellaneous	590	C_{11}	52.0
Miscellaneous polar compounds	500	C_{12}	54.5

A third source of error in the analysis occurs when a material is not chromatographable, that is, it will not pass through the column under the temperature-programming conditions used. To resolve such a situation, liquid chromatography or other methods must be used for these materials. Of all the sources of error in the quantitative analysis, perhaps the most serious is the preliminary workup before injection into the GC.

There were several problems encountered in the identification of the compounds present in the process water extract. First, the mixtures were extremely complex and, despite the high resolution and efficiency of the fused silica capillary columns, not all peaks were resolved. Deconvolution software available on the HP data system cannot handle a large number of spectra. Thus, deconvolution must be done visually; this is not only time-consuming but is also subject to error. Second, there are only a limited number of mass spectra listed in the mass spectra data bases. Often, desired spectra are not available.

Third, there is only a limited number of standard compounds available. In this study, standard compounds were used mostly for quantification. Additional work would be required to verify the proposed characterizations.

Fourth, many of the compounds that were not separated in the liquid-liquid extraction showed up in two or more fractions. This caused additional complications and made analysis difficult.

2.2 OTHER CHARACTERISTICS

Conventional water analyses for various elements were performed on a sample of process water, as reported in Table 2. The water was received in

Table 2 Inorganic Chemistry Analysis of Process Water from Tar Sand Combustion

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
Sodium	2.2	Zinc	0.027
Potassium	2.0	Nickel	0.010
Magnesium	6.6	Arsenic	<0.001
Calcium	24.0	Selenium	0.003
Chloride	15.0	Mercury	0.00015
Fluoride	2.7	Aluminum	0.45
Sulfur	58.0	Lithium	0.002
Cadmium	<0.001	Cobalt	0.004
Chromium	0.003	Molybdenum	0.001
Lead	<0.001	Vanadium	<0.001
Copper	0.031	Barium	0.017
Iron	60	Silver	<0.001
Manganese	0.54	Boron	<0.1

Source: Reference 10.

five epoxy-coated drums and was analyzed for six parameters; the average of these data from the five drums is reported in Table 3. These analyses were performed according to Standard Methods.[9] As indicated by the data, ammonia concentration is below any level that would require stripping in order to avoid ammonia toxicity to the activated-sludge culture. Alkalinity as calcium carbonate equivalent is approximately 100 mg/L, and the raw process water has a relatively low pH of 3.9.

Table 3 Average Concentrations of Selected Parameters in Water Samples[a]

Parameter	Average	Range
pH (units)	3.9	3.9-4.0
NH_3-Nitrogen	49	49-50
Alkalinity (as $CaCO_3$)	107	94-114
COD	2350	2340-2370
TOC	1700	1400-1900
Phenol	19	17-20

[a]Values in mg/L, except for pH.

3 TREATMENT RESULTS

3.1 ORGANIC SOLVENT EXTRACTION

Three organic solvents were tested individually for their efficiency in reducing the organic content of untreated water from tar sand combustion. Varying amounts of isopropyl ether, methyl isobutyl ketone, and hexane were mixed with a constant volume of process water to determine the distribution coefficient (K_d) of the solvent based on COD reductions (see Appendix B for methodology and results). The distribution coefficient is calculated by:

$$K_d = \frac{(W_o - W_1)/V_s}{W_1/V_w} = \frac{C_s}{C_w}$$

where:

K_d = distribution coefficient,

C_s = concentration of COD in solvent (mg/L),

C_w = concentration of COD in water (mg/L),

W_o = initial amount of COD in water (mg),

W_1 = final amount of COD in water (mg),

V_s = volume of solvent (L), and

V_w = volume of water (L).

The average K_d for each of the three organic solvents tested was: isopropyl ether (most polar), 0.42; methyl isobutyl ketone (polar), 1.48; hexane (nonpolar), 1.05. The distribution coefficient for each of the three tested solvents is considered relatively low for use in removing dissolved organic material from water. It should be noted that the samples were heated before COD analysis to ensure removal of residual solvent; this may have caused some loss of volatile constituents other than the solvent. Thus the coefficients reported above are judged to be biased to some extent in favor of solvent extraction. Nevertheless, single-solvent extraction does not appear to be an attractive pretreatment option.

3.2 pH INCREASE AND PRECIPITATION

When the pH was increased to provide suitable conditions for the organisms in the activated-sludge reactor, a noticable "wispy" flocculant material formed and eventually settled within about one day if left undisturbed. Because of the time required for settling, this form of induced coagulation and flocculation was not considered an effective option for prebiological treatment, and the material was not removed before biological oxidation.

If left standing in a laboratory flask for about one day, the flocculant material eventually settled to form a hazy layer at the bottom of the flask. The settled material was not compressed or thickened and could be resuspended easily by a gentle swirl of the flask. The contribution of the

flocculant material to the organic-carbon content can be estimated by comparing total organic carbon (TOC) in the raw process water to soluble organic carbon (SOC) in the activated-sludge influent. These values, 1700 and 726 mg/L, respectively, indicate that the suspended material accounted for about 57% of the organic carbon in the sample.

3.3 BIOLOGICAL OXIDATION WITH ACTIVATED SLUDGE

Activated-sludge treatment is a biological process in which microorganisms are mixed with a nutrient-rich solution in the presence of oxygen to oxidize dissolved organic material. The microorganisms used for initial seeding of the activated-sludge reactor were obtained from previous tests in which the microoganisms had been acclimated to industrial waters that were similarly laden with diverse organic compounds from coal gasification, oil shale, and coking waters.[11-13]

The organisms were allowed to become acclimated to the tar sand water before the data were collected during steady-state conditions. An acclimation period of about 100 days provided ample time to establish relatively steady and representative influent conditions for concentrations of mixed-liquor volatile suspended solids and effluent COD, NH_3, and pH. The raw influent was enriched with 100 mg $NaH_2PO_4 \cdot H_2O$ (31 mg P) per liter of influent, and pH was adjusted with NaOH to a range of about 3.9 to 4.5.

The activated-sludge tank was designed with a self-contained clarifier to allow settling of solids within the system. Oxygen was provided to the reactor by pumping an excess air supply through a sparger located near the bottom of the reactor tank. The air supply and a paddle mixer provided the required conditions for a completely mixed, stirred reactor. The reactor liquor was maintained at room temperature, which varied within the 22-25°C range; dissolved oxygen was maintained at >3 mg/L; and pH in the reactor was maintained at 7.0 to 7.5.

The operating conditions under which the tar sand process water was treated are summarized in Table 4. These data represent average values for a period of about 44 days following the acclimation period.

Data describing the influent and effluent quality at the reactor are provided in Table 5. These results are an average of the data collected during 44 days of operation following acclimation. This sampling period corresponds to a period longer than seven equivalent hydraulic detention times. Analyses for organic carbon in reactor influent and effluent were performed on samples that had been filtered through Whatman No. 41 filter paper; results from these determinations are reported as SOC. The SOC determinations were reported rather than TOC because of potential problems with unrepresentative sampling of suspended organic material.

Table 4 Operating Conditions in the Process Water Activated-Sludge Reactor

Parameter	Value
Mean cell-residence time	40 days
Hydraulic detention time	6 days
Mixed-liquor suspended solids	2594 mg/L
Mixed-liquor volatile suspended solids	2000 mg/L
Food/Microorganism ratio	0.16
BOD reduction factor	0.13 d^{-1}
COD reduction factor	0.14 d^{-1}

Table 5 Performance of Activated-Sludge Treatment on Process Water[a]

Parameter	Influent	Effluent	Percentage of Decrease
Total dissolved solids	333	722[b]	--
Suspended solids	68	34	50
Volatile suspended solids	12	30	--
Chemical oxygen demand	1910	226	88
Biochemical oxygen demand	1660	57	97
Soluble organic carbon	726	90	88
Phenol	14.4	0	100
Kjeldahl nitrogen	2.1	1.9	10
Ammonia (NH_3-N)	48.8	3.6	93
Nitrate (NO_3^--N)	0.5	9.8[b]	--
Thiocyanate (SCN)	1.1	0.5	55
Alkalinity (as $CaCO_3$)	206	61.1	70
Conductivity (μmho/cm)	640	964[b]	51
Color (Pt-Co units)	750	70	91
pH[c]	3.9-4.5	7.0-7.4	--

[a]Values in mg/L, except where noted.

[b]The increases in TDS and in conductivity result from the addition of NaOH to raise influent pH. The increase in nitrate is due to biological oxidation of ammonia.

[c]Influent pH reported as appropriate values before and after pH adjustment. Effluent pH reported as the range recorded during operation.

Mean cell-residence time was maintained by wasting a volume of cells from the mixed liquor that is equal to:

$$W = \frac{(XV/\theta_c) - X_e q}{X}$$

where:

W = sludge volume to be wasted (L/day),

X = concentration of microorganisms in the reactor as mixed-liquor, volatile suspended solids (mg/L),

X_e = concentration of effluent volatile suspended solids (mg/L),

q = waste flow (L/day),

V = reactor volume (L), and

θ_c = mean cell residence time (days).

Following this method of wasting cells to maintain a specific θ_c and θ_H (hydraulic retention time) required that the cells contained in the sludge volume to be wasted (W) be filtered, the filtrate returned to the reactor, and the solids discarded. The cell concentration in the clarifier effluent was accounted for in this wasting scheme.

The influent process water was a light-brown/straw-yellow color that was reduced in color about from 750 to 70 platinum-cobalt units. The water had a "wintergreen" odor that persisted during activated-sludge treatment and was unlike the "pungent" or "musty" odors experienced in conventional activated-sludge treatment.

Operational problems such as frothing or formation of pin-point flocs were not encountered, and sludge settling was good as indicated by the low value of suspended solids in the effluent. The results of treating the tar sand process water by activated sludge indicated that removal efficiencies of 88% for COD and SOC, and 97% for BOD, can be achieved during steady-state operation.

The choice of a six-day θ_H was made primarily on the basis of the research objective, which was to test the feasibility of using activated-sludge treatment with the tar-sand-combustion process water. It is recognized that a θ_H of six days is a longer period than might be economically suitable in a commercial or large-scale facility. The reactor operated at a BOD removal factor of about 0.13 d^{-1} and a COD removal factor of 0.14 d^{-1}. These factors, together with the performance data shown in Table 5, suggest that hydraulic retention time may be reduced to a few days or less.

A base titration curve for a sample of raw R-FC process water is shown in Figure 7. The curve shows that the buffering capacity of the process water is greatest in the range from its original pH of 3.9 to a pH of approximately 5.6. Maximum buffering capacity, as calculated from this curve, is about 0.014 mg/L. Adjustment of the process water pH to a range of 3.9 to 4.5 permitted the activated-sludge system to maintain the pH of its mixed

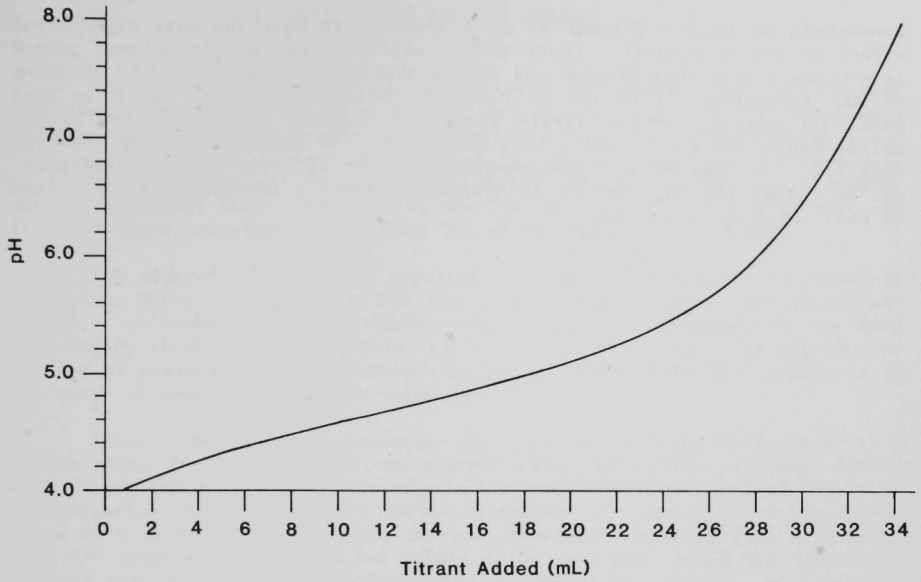


Fig. 7 Base Titration Curve for a Sample of Raw Process Water (Volume: 100 mL; Titrant: NaOH; Normality: 0.06)

liquor at 7.0 to 7.5. As indicated in Figure 7, the amount of base required to provide this pH adjustment is about 1 g NaOH per 5 L of influent process water. This NaOH dose is chemically equivalent to 0.14 g lime (CaO) per liter of influent. Assuming a cost of $55 per ton of delivered (95% pure) lime, the cost of raising the pH to 4.5 would be $33/10^6 gal of influent process water, assuming equal reactivity of caustic and lime. The increase in total dissolved solids and conductivity, as reported in Table 5, is due primarily to the addition of NaOH in order to maintain the pH of the reactor liquor.

Nitrification of the ammonia to nitrate is evident from the data and explains, in part, the reduction in concentrations of ammonia and alkalinity and the increase in that of nitrate. The possibility that the air sparger may strip ammonia from the mixed liquor may also account for some of the decrease in ammonia concentration; this, however, is probably of relative insignificance because the proportion of ammonia at equilibrium with ammonium is relatively small at pH 7. Some ammonia is also metabolized by the microorganisms and then removed by sludge wasting.

Individual pretreatment tests were designed to evaluate the effect of adding cationic and anionic polymers to enhance the settlability of the suspended solids in the process water. The tests were conducted with 100 mL of process water of pH values of 4 and 8 with high doses (1000 to 2000 mg/L) of polymer. The adjustment to pH 8 was made by adding NaOH. Based on the tests

conducted, an anionic polymer at pH 4 appeared to have the most significant effect on solids removal. Under this condition, the anionic polymer seemed to promote a floc that floated and that probably could be removed by skimming or air flotation. Although no turbidity measurements were taken in this test, the clarity of the sample seemed to improve and about half of the solids tended to settle under this condition. In contrast, dosing the process water at high pH with the same polymer, or with the anionic same polymer at either pH, resulted in no apparent effect on immediate or short-term (5 min) settling of solids.

4 ANALYSIS OF ORGANIC CONSTITUENTS

The raw process water was partitioned into acid, base, and neutral fractions by methylene chloride solvent extraction, and these fractions were analyzed by gas chromatography/mass spectrometry (GC/MS). The neutral fraction predominated in concentration among the three components. As reported in Table 6, the neutral fraction contributed 44% of the total extractable/chromatographable (E/C) compounds in the raw water, whereas the acid and base fractions each contributed less than 30% of the total E/C compounds.

The neutral fraction was apparently the most responsive to biological oxidation; Table 6 indicates a 99% reduction in the neutral fraction E/C material. Activated-sludge treatment reduced the E/C compounds in the acid fraction by about 95% and those in the base fraction by 76%. The average reduction of organic material measured as E/C was about 92%; this figure is in the range of removal efficiency found for SOC and COD.

Table 7 and Figure 8 summarize the organic constituents found in each of the three fractions of the raw process water and activated-sludge effluent. The phenols and cresols in the acid fraction represent 67% of the total concentration identified in the influent, whereas the carboxylic acids, which range in size from one to eleven carbons, contribute about 33% of acid fraction E/C compounds. Benzoic and toluic acids were also found and contribute a minor portion of the total identified in the process water. As indicated in Table 7, the higher carboxylic acids tend to be more resistant to biological oxidation. Low-molecular-weight carboxylic acids are biodegradable and are also relatively volatile at low pH values. Because the biological reactor was maintained at a pH of 7.0 to 7.5, removal of low-molecular-weight carboxylic acids was probably a result of biological degradation rather than air stripping. Benzoic and toluic acid compounds and phenols and cresols were removed at greater than 90% efficiency. Carboxylic acids greater in size than 12 carbons were not detected in the sample. This is unusual because aqueous samples from petroleum products range in size beyond C_{12} and there is often a preponderance of C_{16} and C_{18} acids in fossil-derived samples. The pH of the raw process water was 3.9; this may have contributed to insolubility of higher-molecular-weight carboxylic acids in the water. That these compounds were present in the sample but lost during methylene chloride extraction is unlikely because commercial standards of carboxylic acids as large as C_{18} were detected under similar analytical conditions in this study.

The organic compounds in the base fraction of the process water consist primarily of single-ring nitrogen heterocyclics, i.e. pyridine and its alkyl derivatives up to C_7. A smaller proportion of the identified compounds comprised the fused heterocyclic nitrogen compounds, i.e., quinoline and its alkyl derivatives up to C_2. Finally, an extremely small proportion of the process water's base fraction was identified as acridine, a three-ringed nitrogen heterocycle.

The base fraction was apparently the least responsive of the three to biological degradation, with the quinoline group being the most refractory. These compounds were removed at the 75% level, while the pyridines were reduced in the 96 to 100% range. Although acridine appears to have been re-

Table 6 Estimated Concentrations of Extractable/Chromatographable Fractions in Process Water and Activated-Sludge Effluent

Organic Fraction	Process Water Concentration (µg/L)	Fraction of Total (%)	Effluent Concentration (µg/L)	Fraction of Total (%)	Reduction Efficiency (%)
Acid	22,482	29.4	1,226	19.1	94.5
Base	20,453	26.7	4,852	75.6	76.3
Neutral	33,611	43.9	337	5.3	99.0
Total	76,546	100	6,417	100	--[a]

[a]Average reduction efficiency = 91.6%.

duced 87.5% in concentration, the confidence of this number is somewhat lower than others in Table 7 because of the extremely low concentration at which acridine was detected. Thus, the acridines may be even more difficult to degrade biologically than the quinolines.

The identified neutral fraction compounds of the process water consist of unsaturated, oxygenated, cyclic, substituted ketones; oxygenated lactones; and polycyclic inandones. The GC analysis of the neutral fraction of the activated sludge effluent shows practically complete removal of organic constituents in this fraction. Almost all the effluent E/C material in the neutral fraction was present at concentrations lower than 1 µg/L, with a few compounds ranging from 4 to 9 µg/L. Furthermore, none of the effluent peaks was considered to have a close correspondence with the peaks of the process sample, which implies that major neutral-fraction species in the influent were almost completely removed.

Tables 8 through 10 list the compounds in the acid, base, and neutral fractions that were tentatively identified by GC/MS analysis, together with estimated concentrations and GC retention times. Chromatograms of the fractions for each sample are reproduced in Appendix C.

Table 11 compares the estimated total concentrations of the E/C organic constituents with the concentrations of identified E/C organic constituents. The major peaks of the chromatogram were identified, with some exceptions, but identification of the remaining peaks requires alternate analytical approaches such as high-performance liquid chromatography, high-resolution mass spectrometry, and other techniques not used in this study.

Table 7 Summary of Organic Constituents in Process Water and Their Reduction by Treatment with Activated Sludge

Fraction and Constituent	Influent µg/L	Influent % of Total	Effluent µg/L	Effluent % of Total	% Reduction
Acid Fraction					
C_1-C_3 carboxylic acids	54	0.3	--[a]	--	100
C_4-C_6 carboxylic acids	3,718	21.3	13.7	17.6	96.3
C_7-C_{11} carboxylic acids	1,943	11.1	339	43.6	82.6
Phenols/cresols	11,294	64.6	270	34.7	97.6
Benzoic acid	232	1.3	12	1.5	94.8
Toluic acid	253	1.4	20	2.6	92.1
Total	17,494	100	778	100	95.6
Base Fraction					
Pyridine-C_2 pyridines	1817	14.8	10	0.7	99.5
C_3-C_4 pyridines	1718	14.0	68	5.0	96.0
C_5-C_7 pyridines	3028	24.6	275	20.1	90.9
Quinoline-C_2 quinolines	2967	24.2	332	24.3	75.7
C_3-C_4 quinolines	2726	22.2	679	49.7	75.1
Acridine	28	0.2	4	0.3	87.5
Total	12,284	100	1367	100.1	88.9
Neutral Fraction					
Methyl cyclohexenyl ketone	657	4.5	--	--	--
Methyl-methylcyclohexenyl ketone	10,198	70.6	--	--	--
Methyl-tolyl ketone	632	4.4	--	--	--
Acetophenone	591	4.1	--	--	--
Lactones	1,621	11.2	--	--	--
Indanones	748	5.2	--	--	--
Total	14,447	100.0	--	--	--

[a]-- = Not detected.

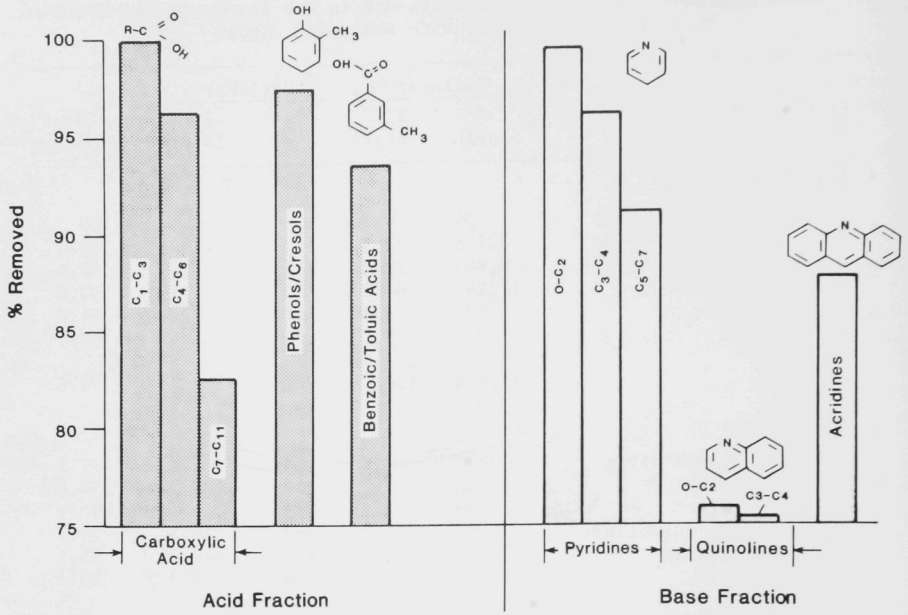


Fig. 8 Removal of Organic Constituents from Process Water by Treatment with Activated Sludge

Table 8 Major Compounds in the Acid Fraction

Retention Time (min)	Tentative Identification	Concentration (µg/L) Influent	Effluent
35.39	Acetic acid	7	-[a]
41.46	Propionic acid	47	-
43.76	Isobutyric acid	312	-
47.58	n-Butyric acid	231	-
50.22	C_5-Carboxylic acid	821	24.2[b]
52.76	C_5-Carboxylic acid	101	-
54.19	n-Pentanoic acid	590	30.6
54.90	C_6-Carboxylic acid	56	-
56.13	C_6-Carboxylic acid	97	7.3
57.53	C_6-Carboxylic acid	201	4.6
58.17	C_6-Carboxylic acid	658	12.4
59.41	C_6-Carboxylic acid	48	-
60.56	n-Caproic acid	603	58.2
62.82	C_7-Carboxylic acid	78	5.3
63.05	C_7-Carboxylic acid	81	-
63.62	C_7-Carboxylic acid	149	0.8
63.94	C_7-Carboxylic acid	175	4.6
64.91	C_7-Carboxylic acid	93	5.8
66.36	n-Heptanoic acid	451	84.7
67.06	C_8-Carboxylic acid	30	2.0
67.53	C_8-Carboxylic acid	25	7.3
67.71	C_8-Carboxylic acid	40	3.7
68.33	Phenol	1845	22.9
68.52	o-Cresol	1886	15.3
70.37	C_8-Carboxylic acid	97	18.3
71.85	n-Caprylic acid	285	77.2
72.23	C_2-Phenol	1735	22.7
72.54	m- and p-Cresol	2536	36.8
75.53	C_2-Phenol	751	21.2
76.74	C_2-Phenol	827	25.2
77.04	n-Pelargonic acid	284	66.1
78.41	C_3-Phenol	295	57.1
78.74	C_3-Phenol	526	24.3
79.10	C_3-Phenol	451	41.4
80.78	C_3-Phenol	121	-
81.93	n-Capric acid	155	63.0
82.41	C_3-Phenol	146	-
85.20	C_3-Phenol	156	2.3
86.71	n-Undecylic acid	19	2.2
87.45	Benzoic acid	232	11.8
91.62	Toluic acid	146	15.0
92.92	Toluic acid	107	5.4

[a]- = Not detected.

[b]Decimal accuracy is reported for comparison of concentrations within the particular column.

Table 9 Major Compounds in the Base Fraction

Retention Time (min)	Tentative Identification	Concentration (µg/L)	
		Influent	Effluent
14.98	Pyridine	444	5.5[a]
16.99	2-Methyl pyridine	277	-[b]
19.69	C_2-Pyridine	229	-
22.54	3-Methyl pyridine	310	-
23.05	4-Methyl pyridine	181	-
24.16	C_3-Pyridine	40	1.9
24.88	C_3-Pyridine	55	-
25.12	C_4-Pyridine	34	0.4
26.10	C_2-Pyridine	142	2.1
26.91	C_2-Pyridine	234	2.0
28.51	C_4-Pyridine	179	5.4
29.60	C_3-Pyridine	189	2.7
29.76	C_3-Pyridine	54	-
30.52	C_3-Pyridine	17	0.5
30.73	C_3-Pyridine	196	1.3
31.18	C_3-Pyridine	100	2.5
31.60	C_3-Pyridine	60	1.2
31.80	C_3-Pyridine	65	6.8
32.20	C_3-Pyridine	27	3.2
32.40	C_4-Pyridine	119	14.1
33.03	C_5-Pyridine	69	1.7
33.24	C_4-Pyridine	201	2.0
33.95	C_3-Pyridine	35	2.7
34.68	C_5-Pyridine	263	9.0
34.85	C_5-Pyridine	206	
35.75	C_4-Pyridine	119	10.0
35.92	C_4-Pyridine	88	
36.59	C_6-Pyridine	283	16.9
37.52	C_4-Pyridine	85	9.2
37.73	C_4-Pyridine	55	4.4
38.26	C_6-Pyridine	77	-
38.51	C_5-Pyridine	155	13.6
38.96	C_5-Pyridine	117	14.3
39.19	C_5-Pyridine	92	
39.82	C_6-Pyridine	94	11.0
40.50	C_6-Pyridine	213	14.0
40.88	C_6-Pyridine	109	6.1
42.95	C_5-Pyridine	324	46.7
43.37	C_7-Pyridine	133	8.6
43.93	C_5-Pyridine	38	10.1
44.24	C_6-Pyridine	157	11.3
44.34	C_6-Pyridine	110	12.8
44.87	C_6-Pyridine	102	8.8
45.47	C_6-Pyridine	90	-
45.64	C_6-Pyridine	78	-
46.36	C_5-Pyridine	201	58.7
48.17	C_6-Pyridine	117	31.1

Table 9 (Cont'd)

Retention Time (min)	Tentative Identification	Concentration (µg/L) Influent	Effluent
63.72	Quinoline	719	16.2[a]
65.06	Methyl quinoline	92	51.7
65.28	Methyl quinoline	76	47.1
65.70	Methyl quinoline	665	37.2
67.08	Methyl quinoline	101	-
68.62	C_2-Quinoline	154	34.5
69.76	C_2-Quinoline	381	42.6
70.73	C_2-Quinoline	46	21.2
71.55	C_2-Quinoline	344	19.5
72.38	Methyl quinoline	233	23.7
73.29	C_2-Quinoline	130	13.9
73.45	C_3-Quinoline	67	12.7
73.77	C_3-Quinoline	110	15.1
74.15	C_3-Quinoline	420	73.7
74.29	C_3-Quinoline	181	
74.49	C_3-Quinoline	52	27.8
74.85	C_2-Quinoline	26	24.6
75.21	C_3-Quinoline	37	27.2
75.66	C_3-Quinoline	109	46.5
75.97	C_4-Quinoline	25	17.2
76.43	C_3-Quinoline	107	18.8
76.89	C_4-Quinoline	29	12.6
77.19	C_3-Quinoline	27	7.9
77.51	C_3-Quinoline	62	13.2
77.93	C_3-Quinoline	54	-
78.07	C_4-Quinoline	99	25.5
78.84	C_4-Quinoline	164	68.1
79.16	C_4-Quinoline	39	9.2
79.47	C_4-Quinoline	316	52.3
79.69	C_4-Quinoline	111	50.4
80.01	C_4-Quinoline	20	12.9
80.43	C_4-Quinoline	103	10.3
81.16	C_4-Quinoline	78	25.7
81.37	C_4-Quinoline	40	9.2
81.55	C_4-Quinoline	27	9.0
81.76	C_4-Quinoline	62	23.2
84.51	C_4-Quinoline	44	5.5
85.12	C_3-Quinoline	62	8.9
86.31	C_4-Quinoline	52	29.7
86.71	C_4-Quinoline	60	9.8
87.35	Acridine	28	3.5
87.73	C_4-Quinoline	146	47.6
88.04	C_4-Quinoline	23	8.9

[a]Decimal accuracy is reported for comparison of concentrations within the particular column.

[b]- = Not detected.

Table 10 Major Compounds in the Neutral Fraction

Retention Time (min)	Tentative Identification	Concentration (µg/L) Influent	Effluent
35.19	Methyl cyclohexenyl ketone	333	-[a]
36.18	Methyl-methylcyclohexenyl ketone	250	-
37.86	Methyl-methylcyclohexenyl ketone	296	-
38.43	Methyl cyclohexenyl ketone	115	-
41.64	Methyl-methylcyclohexanyl ketone	4809	-
43.04	Methyl-methylcyclohexanyl ketone	4607	-
43.98	Acetophenone	591	-
46.20	Hexanoic acid lactone	310	-
46.83	Hexanoic acid lactone	225	-
49.35	Heptoic acid lactone	501	-
49.54	Heptoic acid lactone	271	-
53.40	Methyl-tolyl ketone	187	-
53.60	Methyl-tolyl ketone	179	-
54.50	Methyl-tolyl ketone	266	-
56.01	Lactone	209	-
55.54	Lactone	105	-
56.01	Methyl cyclohexanyl ketone	209	-
62.69	Methyl-methylcyclohexanyl ketone	138	-
63.71	Methyl-methylcyclohexanyl ketone	98	-
67.31	Indanone	189	-
68.21	Dihydroindanone	154	-
70.23	Dihydroindanone	169	-
77.01	Methyl dihydroindanone	114	-
77.43	Dihydroindanone	122	-

Note: Organic constituents in neutral fraction of effluent were present in concentrations of less than a few ug/L.

[a]- = Not detected.

Table 11 Concentrations of Total Extractable/Chromatographable and Identified Organic Constituents in Process Water (µg/L)

Source and Fraction	Total Extractable/ Chromatographable	Total Identified
Influent		
Acid	22,482	17,494
Base	20,453	12,284
Neutral	33,611	14,447
Effluent		
Acid	1,226	778
Base	4,854	1,367
Neutral	337	0

5 MUTAGENICITY TESTING

As part of the characterization effort, the sample of raw process water was analyzed for mutagenicity by the standard Salmonella/Ames test. This extremely sensitive and simple test makes use of cultures of mutant bacterial strains to detect chemically induced reverse mutation.[14]

Much evidence is available to indicate that, with few exceptions, carcinogens are mutagens. Studies that have characterized the mutagenic tendencies of synthetic fuel products from technologies such as oil shale retort, coal gasification, and coal liquefaction indicate that the mutagenicity of most oils derived from synthetic fuel technologies is significant.[15]

5.1 DESCRIPTION OF TEST

Five strains of the bacterium Salmonella typhimurium described by Ames, McCann, and Yamasaki[16] have different types of histidine mutagenesis: strain TA1535, base pair substitutions; strains TA1537 and TA1538, frameshift mutagenesis. These strains have two additional mutagenic tendencies that promote the sensitivity of the cells to mutagens: "...one causes loss of the excision repair system and the other loss of the lipopolysaccharide barrier that coats the surface of the bacteria".[17] The lipopolysaccharide normally coats these bacteria and serves as a barrier to mutagens that otherwise could penetrate the cell membrane.[18] This cell layer is not found in mammalian cells. Strains TA98 and TA100 were developed from strains TA1538 and TA1535, respectively, and contain a resistance transfer factor (R factor). These two strains are also much more sensitive to a number of carcinogens that are only weakly apparent with the original strains. In addition, certain plasmids increased the rates of ultraviolet-induced mutation.[19] As a result of the mutations, the Salmonella strains are unable to produce their own histidine and thus cannot survive and replicate without a supplemental source of histidine. A minimal amount of histidine is added to the growth media in the test to promote a limited amount of growth and to detect the microscopic cells in a monocolony on a petri dish.

In the procedure, the test chemical or substance is added to the growth media under carefully controlled conditions. When the chemical or substance in question is mutagenic, some of the cells that it contacts revert to produce their own histidine and are then able to express themselves in their reproduction as visible colonies on the petri dish. When the colony count of the revertants is statistically greater than the control count, the chemical or substance is considered mutagenic. Ames et al.[16] reported an average natural revertant mutation in the control count of 40 and 160 revertants/plate with TA98 and TA100, respectively. Slightly larger numbers of spontaneous revertant colonies are detected on plates containing a rat liver enzyme homogenate, referred to in the test as S9.[20]

Some mutagens, such as aromatic amines and polycyclic hydrocarbons, are carcinogenic to humans when they are activated by liver enzymes. Bacteria do not duplicate the mammalian metabolism and, in particular, do not produce enzymes similar to mammalian enzymes that activate a significant chemical group. For these reasons, the addition of S9 homogenate of liver

enzymes prepared from rats (or humans) is incorporated into the Ames test to introduce an important aspect of mammalian metabolism into the in vitro test.

The raw process water was examined for its mutagenic tendencies with the Salmonella/Ames test. The tests were conducted according to the overlay method of Ames, McCann, and Yamasaki.[15] All tests were conducted using 0.2 μL/plate of S9 (0.04 mL of S9 per mL of mixture). The positive control test for insuring the integrity of the test cultures indicates revertant counts of 140 and 298 counts per plate for TA98 and TA100 strains. The control substance was benzo(a)pyrene at a dose of 1 μg/plate.

5.2 RESULTS

The number of revertants on the plates used to test the process water is not considered statistically greater than that of the control plates (Table 12). Therefore, tar sand process water is not characterized as mutagenic according to the screening test.

The results of this single test, however, should not be considered an absolute indication that the process water is nonmutagenic or noncarcinogenic. Although the Salmonella/Ames test has been proved effective in detecting the mutagenicity of single compounds, the effectiveness of the test in evaluating complex organic and inorganic mixtures such as those occurring in the process water has not been demonstrated. Some mixtures inhibit bacterial response to known mutagens, and thus the mutagenic nature of the material is masked. The Salmonella/Ames test may therefore be considered a screening test; additional examination of the process water by other available mutagen tests should be done in order to increase the confidence level of the designated "nonmutagenic" qualities.

Table 12 Results of Salmonella/Ames Test on Tar Sand Process Water Influent

Sample	Concentration (μL/plate)	Counts/Plate[a]			
		TA98		TA100	
		-S9[b]	+S9[c]	-S9	+S9
Control	--	18	41	99	100
Influent	10	19	35	123	131
Influent	100	31	27	123	124

[a]Means of duplicate samples.

[b]Without S9.

[c]With S9.

Plans for introducing a new or unique material, such as the tar sand process water, to the environment raise legitimate questions with regard to mutagenicity, carcinogenicity, and the protection of public health and the environment. A battery of appropriate tests, including those for toxicity using various species, should be performed. Because each test system detects a few carcinogens that others do not, the idea of a battery of short-term tests is now favored by many investigators. "The National Cancer Institute has recently published criteria for (an) adequate carcinogenicity test. The test should be of adequate size and duration (lifetime preferred in rodents), in at least two animal species, at several dose levels, and positive controls should be of the same general chemical type as the chemical under test."[21]

The Samonella/Ames test has a remarkably high (90%) ability to indicate mutagenicity of a carcinogenic compound;[22] this criterion is therefore used to justify the appropriateness of the test. Much discussion appears in numerous publications to explain the occurrence of "false positives" and "false negatives" in the test.[21,23] These explanations usually relate to the unique biochemical differences between mammals and bacteria in the case of "false negatives" and to the incompleteness of carcinogenic studies that may eventually show a decrease in "false positives" when more comprehensive carcinogenic testing with animals is completed.

6 CONCLUSIONS, DISCUSSION, AND RECOMMENDATIONS

This research provides a comprehensive evaluation of the organic constituents of reverse-forward combustion process water and their specific removal efficiencies by activated-sludge treatment. The results of this study can serve as a base to which data can be added in order to answer environmental science and engineering questions regarding water-related problems of tar sand extraction.

The study disclosed that process water from tar sand combustion contains organic material consisting of a wide variety of oxygenated, unsaturated, and heterocyclic compounds that can be removed with relative ease by activated-sludge treatment. Of the compound groups tentatively identified, only the quinolines and higher molecular weight carboxylic acids appear to be comparatively refractory to this treatment. The treatment resulted in good solids-settling characteristics. In addition, color reduction and nitrification of the influent ammonia were apparent. High removal efficiencies were reported for BOD, COD, and SOC. The sampled water was not found to be mutagenic, as tested according to the standard protocol of Salmonella/Ames.

It is not certain what defines a representative aqueous sample derived from tar sand combustion. Because water quality would probably vary during the combustion period, an approximate sample composition or treatment cannot be specified until more information is available on the variations in water quality. The water sample evaluated in this research had been stored in cold conditions for a relatively long time. It is not clear how this affected the quality of the water or the type and concentration of solids suspended in the water. These factors should be considered in any additional treatability and characterization studies of process water from tar sand combustion.

Additional work must be performed in order to obtain a more complete organic characterization of constituents. Analytical techniques such as high-performance liquid chromatography and high-resolution mass spectrometry can be employed to resolve the identity of some of the minor but prevalent types of chromatographable compounds. Nonetheless, this would still leave a large fraction of organic material to be characterized.

If reverse-forward combustion were eventually considered to be an economical process for recovering the energy content of tar sand deposits, a more comprehensive research effort would be recommended in order to:

1. Insure the environmental acceptability of the process water.
2. Make a technical assessment of alternative treatment methods in order to establish an effective and economical water-management system for the production process.

A more comprehensive investigation would include additional studies of toxicity and water management. Water-management studies must consider alternatives for process water recycling, reuse, and discharge, as well as for engineering design and cost analysis. Activated sludge has been shown to be an

efficient treatment for tar sand process water. Various physicochemical treatment strategies, including chemical coagulation and precipitation, should also be evaluated.

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APPENDIX A

PREPARATION PROCEDURE FOR TAR SAND WATER SAMPLES

APPENDIX A

PREPARATION PROCEDURE FOR TAR SAND WATER SAMPLES

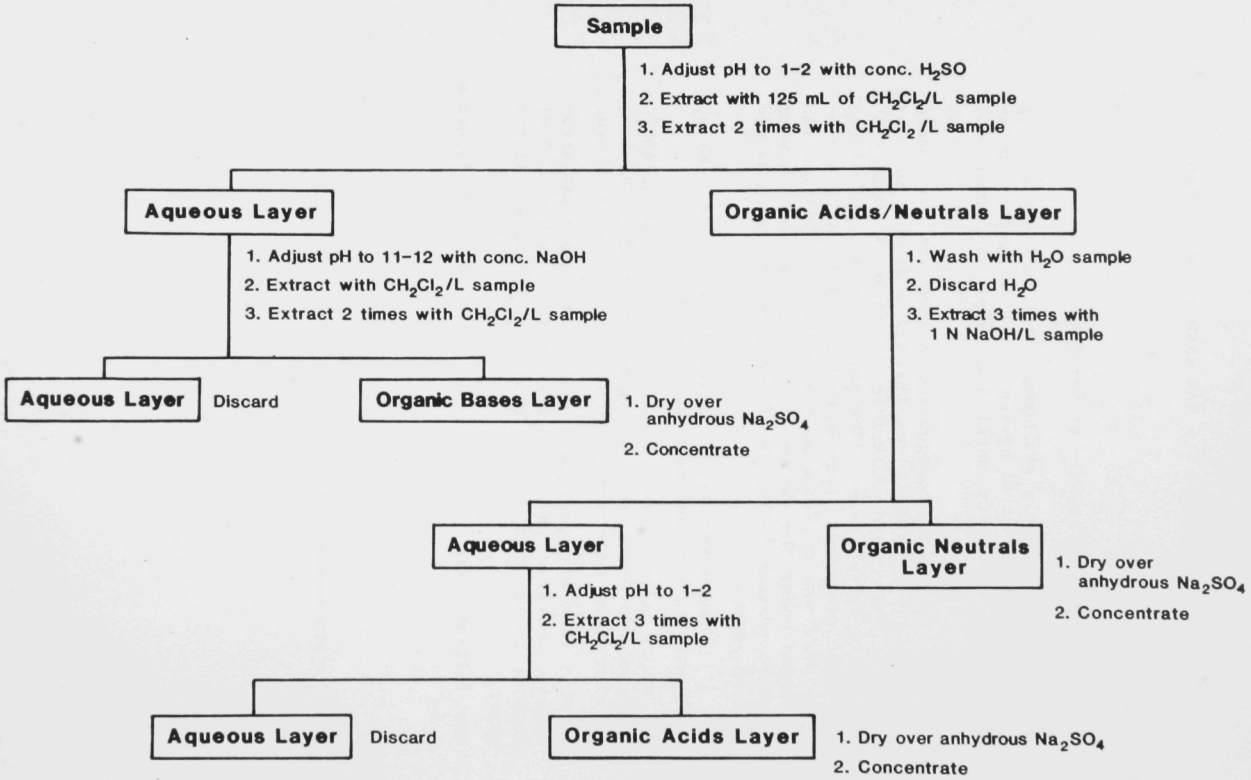
A.1 PROCEDURE

The process water samples were prepared as follows:

1. Each wastewater sample was homogenized in the glass jug in which it was received by vigorous shaking for approximately one minute or until the sample appeared well mixed.
2. A 300-mL volume of homogenized sample was accurately measured and then filtered through a 30-mL, medium-porosity, Pyrex gooch crucible fitted with "Mead Flo" fiberglass filter paper. The gooch crucible and filter paper had previously been heated at 110°C until a constant mass was obtained and recorded. Filtration was performed under the vacuum created by a mechanical pump (<2 torr pressure). The pH of the filtrate was measured with pH paper.
3. The filtered material was dried in a drying oven at 110°C until a constant mass was obtained.
4. The dried filtered material was then muffled at 450°C overnight to drive off all organic material. The mass of inorganic material present was then determined.
5. A 2-L volume of homogenized wastewater sample was accurately measured and then filtered through a 150-mL Buchner funnel fitted with "Mead Flo" fiberglass filter paper.
6. The filtrate was fractionated as indicated in Figure A.1.

A.2 RESULTS

The results are summarized in Table A.1.



Note: A 500-mL Kuderna-Danish apparatus was used to concentrate the acid, base, and neutral fractions. Final volumes were obtained under a stream of nitrogen.

Fig. A.1 Flow Diagram of Solvent Extraction

Table A.1 Results of Samples Preparation

Parameter	Influent	Effluent
Constant mass of crucible, filter paper, and solids (a)	32.14806 g	32.08230 g
Constant mass of the above after muffling (b)	32.12493 g	32.07597 g
Constant mass of crucible and filter paper (c)	32.07755 g	32.07662 g
Volume of sample wastewater filtered (d)	285 mL	275 mL
Mass of suspended solids (a - c = e)	0.07051 g	0.00568 g
Weight of suspended solids/liter of sample (e/d)	247.4 mg/L	20.7 mg/L
Mass of inorganic solids (b - c = f)	0.04730 g	0 g
Weight of inorganic solids/liter of sample (f/d)	166.2 mg/L	0 mg/L
Initial pH of filtrate	5	5
Volume used for extraction of liquid	2275 mL	2225 mL
Volume of filtrate fractions		
Neutral	5.0 mL	6.0 mL
Acid	5.0 mL	8.0 mL
Base	8.0 mL	6.0 mL

APPENDIX B

SOLVENT EXTRACTION METHODOLOGY AND RESULTS

APPENDIX B

SOLVENT EXTRACTION METHODOLOGY AND RESULTS

B.1 WATER SAMPLE

Volume	250 mL
COD	2250 mg/L
pH	4.0

B.2 SAMPLE PREPARATION

1. Pour 250 mL of process water into each of six 500-mL separatory funnels.
2. Add 0, 50, 100, 150, 200, and 250 mL of solvent to each funnel.
3. Mix the sample with the organic solvent by inverting the funnel 50 times. Fifty simple inversions on each sample.
4. Separate the water phase from the solvent after allowing the funnel to stand for 10 minutes.
5. Heat water phase under partial vacuum to insure complete removal of solvent. Perform GC analysis to confirm removal of residual solvent.
6. Determine COD reduction.

B.3 DATA RESULTS

The results are summarized in Table B.1.

Table B.1 Results of Solvent Extraction

Solvent	Solvent Volume (mL)	Final Sample COD (mg/L)	Calculated Distribution Coefficient (K_d)
Isopropyl ether	50	1904	0.92
	100	2054	0.24
	150	1890	0.32
	200	1758	0.35
	250	1757	0.28
Methyl isobutyl ketone	50	1428	2.89
	100	1207	2.17
	150	1640	0.62
	200	1261	0.98
	250	1279	0.76
Hexane	50	1626	1.93
	100	1526	1.19
	150	1616	0.66
	200	1240	1.02
	250	1572	0.43

APPENDIX C

CHROMATOGRAMS OF ACID, BASE, AND NEUTRAL FRACTIONS FROM INFLUENT AND EFFLUENT OF ACTIVATED-SLUDGE TREATMENT

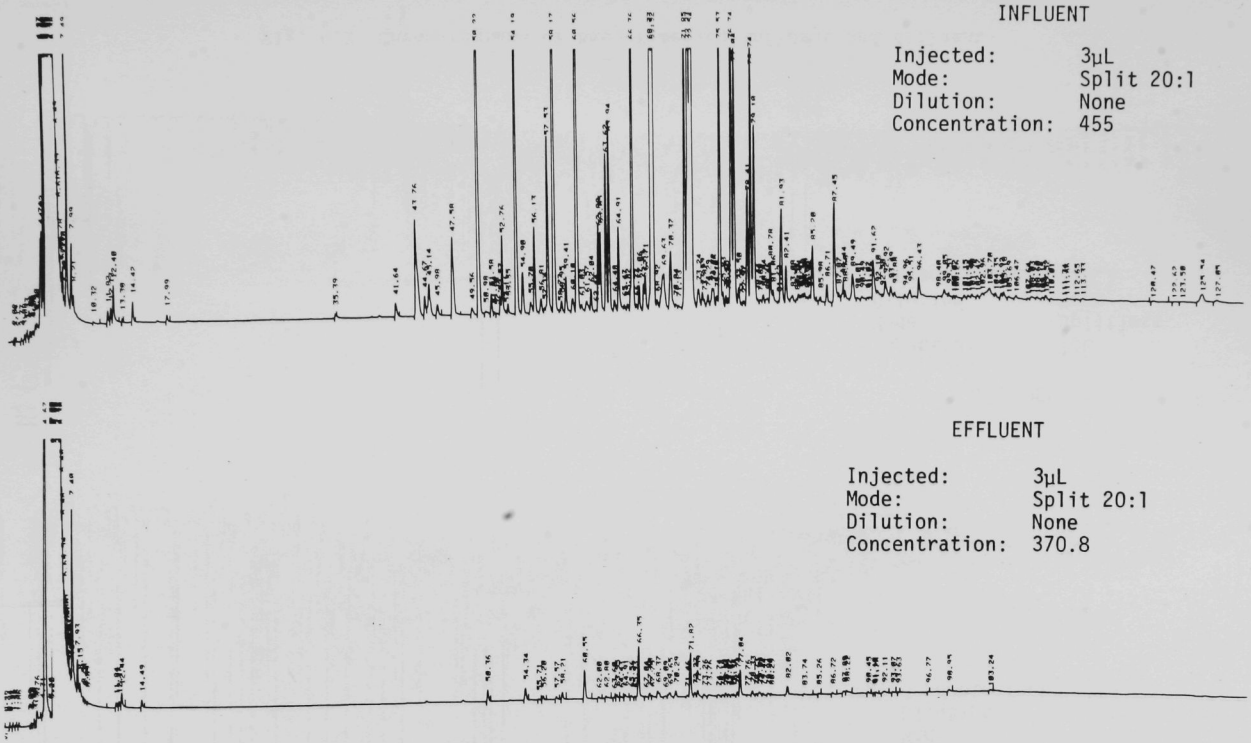


Fig. C.1 Chromatograms of Acid-Fraction Influent and Effluent

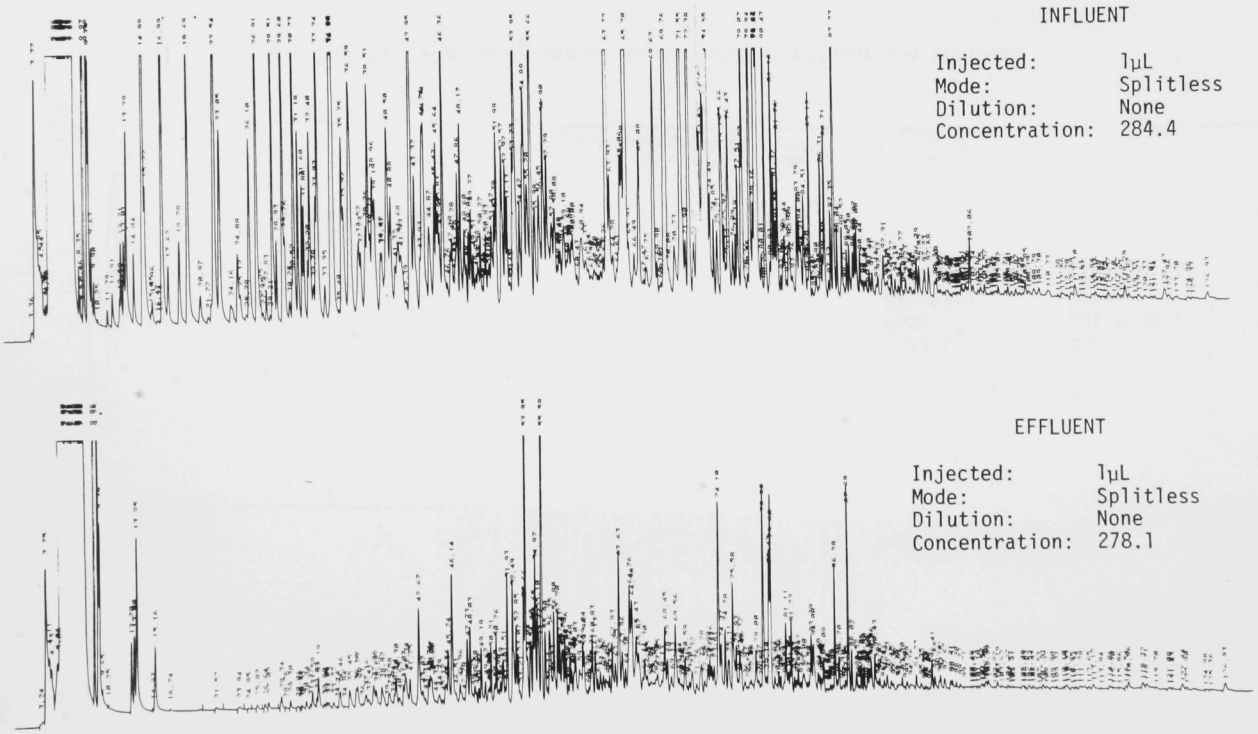


Fig. C.2 Chromatograms of Base-Fraction Influent and Effluent

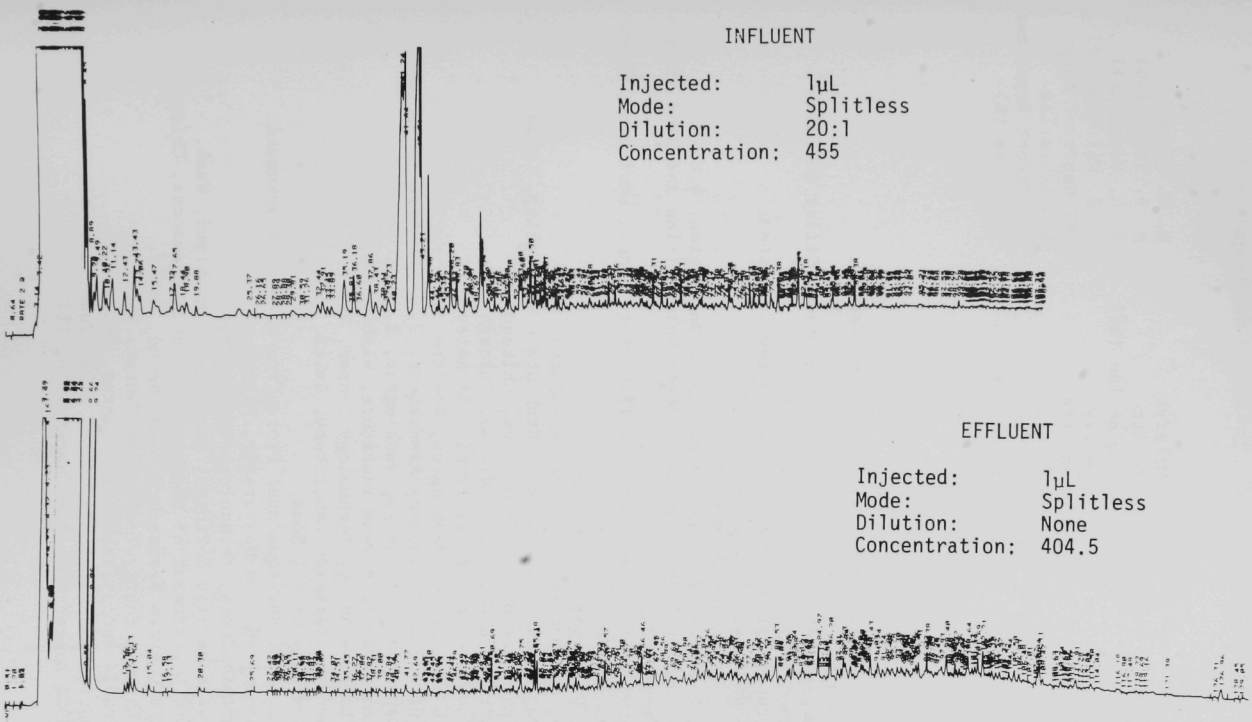


Fig. C.3 Chromatograms of Neutral-Fraction Influent and Effluent

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